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Dielectric Properties and Morphology of Ferroelectric Ceramic-Polymer Composite Films

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ABSTRACT

Dielectric constant and morphology of $BaTiO_3$-polymer composite films were studied as a function of the filler concentration. The morphology of the films was examined using laser scanning confocal microscopy, which is capable to measure small particle distributions in more details than conventional microscopy. The thin-slice images allowed us to visualize the micron-size particles and the polymer between them nondestructively. We have found that, although $BaTiO_3$ particles appear to form clusters at low filler concentrations, the cluster formation does not affect the dielectric constant of the composites.

INTRODUCTION

High dielectric constant (High-K) ferroelectric ceramic-polymer composites have become potential candidate materials for integration into high frequency electronics. Detailed understanding of this class of materials will help electronic industry in planning, design and processing of these materials. We have synthesized a series of $BaTiO_3$-polymer composites and measured their dielectric properties over a wide volume fraction of $BaTiO_3$ filler [1]. $BaTiO_3$ has been selected, because it is the best known ferroelectric ceramics. We have used photo-polymerization method to keep the processing conditions simple and to obtain the composites as voids-free, two-component systems.

In this paper, we report the microstructure of a series of composites, observed using laser scanning confocal microscopy (LSCM). There is much advantage in the use of LSCM over conventional microscopy techniques.[2,3] The LSCM affords visualization of smaller features than the conventional microscopy and with a better depth resolution, which allowed us to study the composite microstructure in details.

EXPERIMENTAL

Materials

Trimethylolpropane triacrylate (TMPTA monomer) was purchased from Monomer Polymer & Dajac Labs. Barium titanate powder ($BaTiO_3$ filler) and 2,2-dimethoxy-2-phenylacetophenone (photoinitiator) were obtained from Aldrich. All materials were used as received.[4]

Sample Preparation

First, 1 % solution of the photoinitiator in the monomer was prepared. Next, barium titanate powder was mixed into the solution to form liquid formulations of various filler concentrations. The formulations were cured by exposure of a few drops of each formulation squeezed between microscope slides to UV-light. During the exposure, the slides were kept at a constant distance of about 100 μm using self-adhesive labels in the role of spacers. The cured composites did not adhere strongly to the glass and were carefully separated from the slides in the form of thin films. So prepared films were examined directly by the laser scanning confocal microscopy. For dielectric measurements, circular aluminum electrodes, 12.7 mm in diameter, were vacuum-deposited on both sides of the composite films to form parallel-plate capacitors. In this way, we prepared a series of $BaTiO_3$-polymer composites with $BaTiO_3$ volume fraction of 5%, 10%, 15%, 20%, 25%, 30%, and 35%.

Measurements

A Zeiss Laser Scanning Confocal Microscope Model LSM510a was applied to characterize the microstructure of the composite wafers. The wavelength of the laser was 543 nm with the bandwidth of 10 nm. Each confocal micrograph covered the scanning area of about 18.4 μm × 18.4 μm. An oil immerge objective (100/1.3) was used for the refractive index matching with the polymer matrix. The objective numerical aperture was 1.3, which provided the transverse and depth resolutions of 155 nm and 286 nm respectively at the laser wavelength applied. Several LSCM optical slices at various focal plane distances from the sample surface were collected for each composition. The LSCM images shown in this paper are 2D intensity profile presentations of overlapping optical slices (i.e., stacks of several z-scan images in 2D projection with z = 1 μm per z-step).

Dielectric measurements were performed with Hewlett-Packard 4194A Impedance/Gain-Phase Analyzer, at 25 ^{o}C. The dielectric constant of the composites was calculated from the capacitor geometry and their capacitance. The dielectric data reported in this paper refer to the frequency of 1 kHz. The combined standard uncertainties of these data were estimated to be at the level of 10 % of the measured values.

RESULTS AND DISCUSSION

Figure 1 illustrates LSCM images of the 2D projections of $BaTiO_3$-polymer composites containing 5 % to 35 % of $BaTiO_3$ powder by volume. While in traditional transmission microscopy, even at 5 % $BaTiO_3$ content, the $BaTiO_3$/polymer composite films always appeared to be uniform, a clear difference in the particle distribution is observed under the LSCM (Fig.1). This results from the fact that a conventional microscope usually covers much thicker layer than that imaged by LSCM. The LSCM utilizes coherent light and collects light exclusively from a single plane (i.e., a pinhole slit conjugated to the focal plane), while rejecting the light out of focal plane. Thus, by moving the focal plane location along z-axis, optical slices up to certain depth from the sample surface can be visualized separately. As there is a large contrast in light scattering cross-section between the $BaTiO_3$ particles and the polymer matrix, LSCM provides a non-destructive, powerful visual aid for characterizing particles distribution in $BaTiO_3$/polymer composites. Using LSCM we observe that at small concentrations $BaTiO_3$ particles have

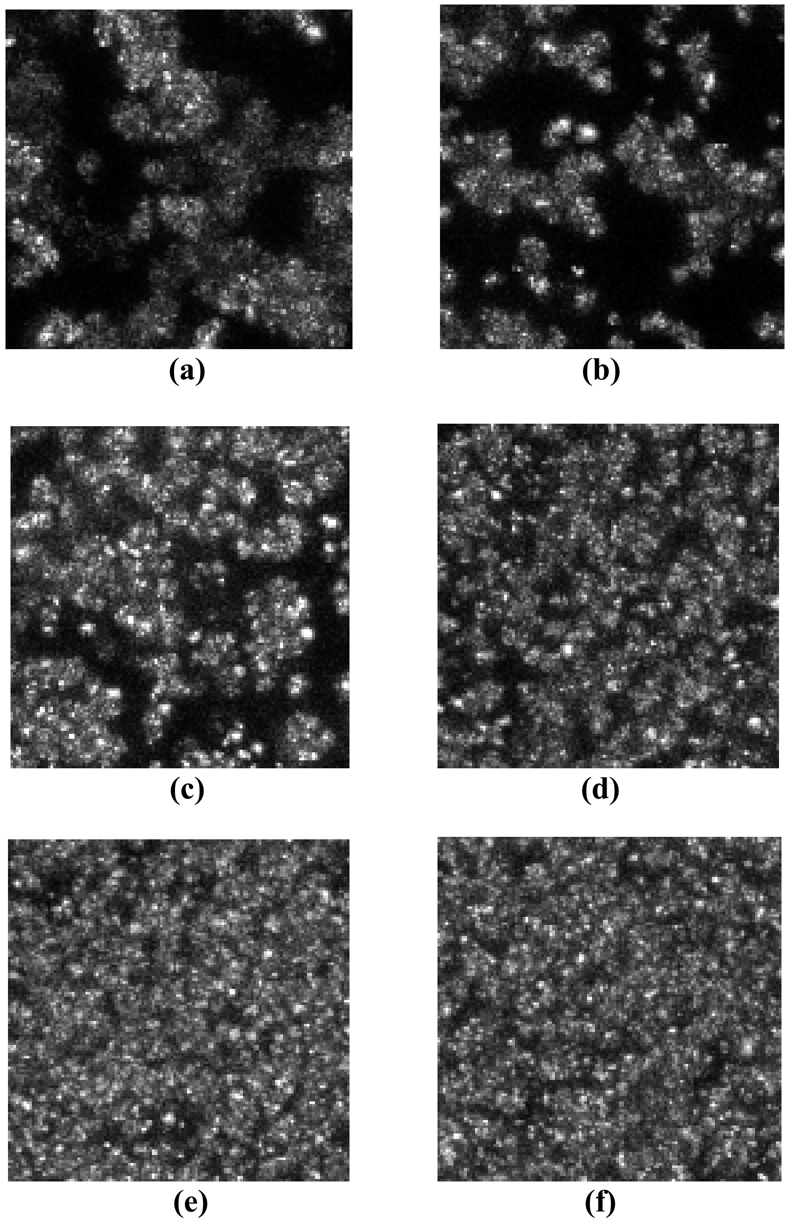

Figure 1. LSCM 2D-projection images of $BaTiO_3$ particle distribution in TMPTA polymer matrix. The volume fraction of $BaTiO_3$ in the films are (a) 5 %, (b) 10 %, (c) 15 %, (d) 20 %, (e) 25 %, and (f) 35 %.

tendency to form clusters. As the concentration increases, the clusters coalesce into more uniform structures. Consequently, $BaTiO_3$ particles appear to be better dispersed in the high concentration composites than at low concentrations. Detailed LSCM images showed that the size of $BaTiO_3$ particles was in the range of 0.5 - 1 μm with a relatively narrow size distribution.[5] Since the same powder was used to make all films, the particle size was the same. Only the size of clusters is different. To render a preliminary quantitative index for these microstructure features, we measured the size of clusters. Figure 2 shows the plot of the median cluster size as a function of $BaTiO_3$ concentration. The cluster size decreases with increase of $BaTiO_3$ content. At about 25 % of $BaTiO_3$ by volume, the cluster size reached the limit of the particle size.

In our previous work,[1] we studied dielectric properties of a series of $BaTiO_3$-polymer composites and we found that for composites with random particle distribution, the relationship between logarithm of dielectric constant of the composites and volume fraction of the filler is linear over a broad range of frequencies. The dielectric constant appears to have a strong concentration dependence. From the microstructure data it might appear there could be a deviation from regularity of properties change at the level of 25 % of $BaTiO_3$, because of different microstructure of the composites at high $BaTiO_3$ concentrations compared to that at the low concentrations. Hence, we have measured the dielectric constant of these series of polymer composites and plotted the data in Figure 3 for comparison. Figure 3 indicates the logarithm of dielectrics constant of the $BaTiO_3$-polymer composites still is proportional to the volume fraction of $BaTiO_3$ filler over the entire range of the concentrations studied with no significant deviation

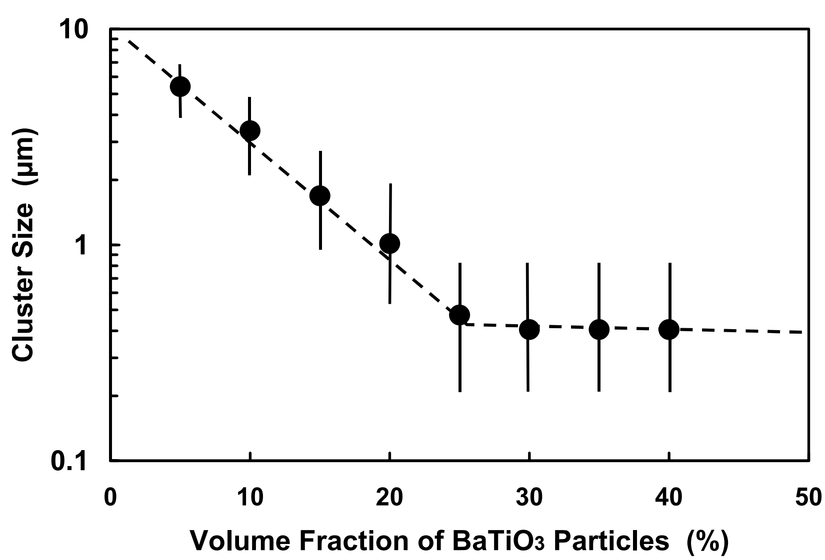

Figure 2 The median size of $BaTiO_3$ clusters as a function of $BaTiO_3$ volume fraction. The dashed line is just for visual guidance.

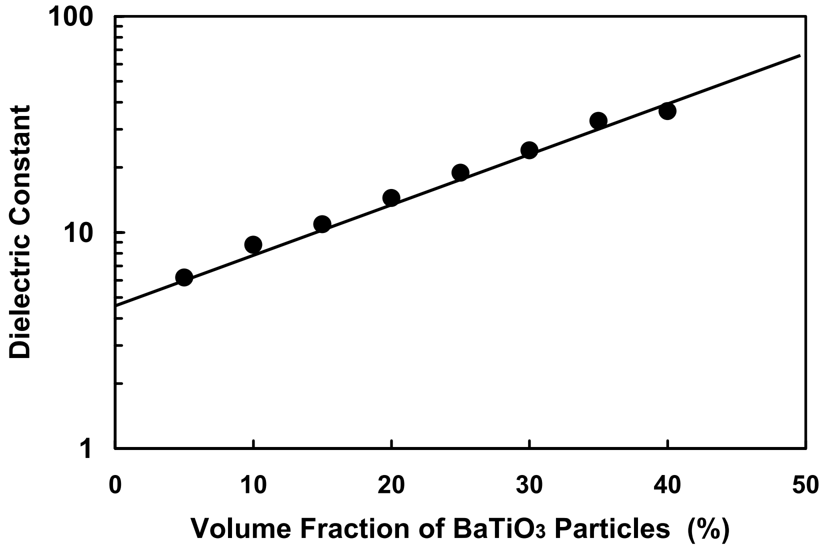

Figure 3 Dielectric constant of $BaTiO_3$ polymer composite films as a function of volume fraction of $BaTiO_3$ particles.

from the relationship linearity. Hence, the slight non-uniformity of particle distribution caused by cluster formation does not affect macroscopic dielectric properties of the $BaTiO_3$-polymer composites.

CONCLUSIONS

LSCM images of the microstructure of $BaTiO_3$-polymer composites have revealed that $BaTiO_3$ particles form clusters at low particle concentrations. The diameter of the cluster was up to 10 µm at 5 % volume fraction of $BaTiO_3$. The cluster size decreases with increase of the particle concentration. Above 25 % the particle distribution appears to be uniform. The dielectric constant of the composite films is not affected by the underlying topological variations. The possible reason is that the sensing electric field has much longer wavelength than the physical dimensions of the particles and clusters.

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